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### **Graphical abstract**

## Hydroxyapatite nanoparticles on dendritic $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hierarchical architectures for heterogeneous photocatalyst and adsorption of Pb(II) ions from industrial wastewater

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#### Abstract

A facile surfactant free hydrothermal process was used to prepare dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and hydroxyapatite (HAp) nanoparticles dispersed on the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures. The dendrite consists of 1 µm long central trunk with the secondary branches of 80 nm. The prepared nanocomposite with mesoporous structure exhibits a high specific surface area. A possible formation mechanism for the dendrite is proposed. These HAP/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposites were further used to degrade the methyl violet (MV) dye using photodegradation and adsorb the Pb(II) ions from the industrial waste water through the adsorption process. These investigations clearly confirm the extremely fast degradation and adsorption of dye and Pb (II) ions from the aqueous solution. The result confirms the new method having advantages of both photodegradation and adsorption process for the removal of various wastewater pollutants. The present method is more energetic, cost effective, sustainable and also easily recycled after adsorption process with the high recovery ratio due to the magnetic response of the nanocomposite.

#### 1. Introduction

Recently, the utilization of nanomaterials for environmental remediation has attracted much attention due to their improved specific surface area for excellent adsorption and degradation. The expansion of industrial and agricultural activities severely contaminates the water, air and soil with heavy metal ions, toxic gases and organic pollutants. Among these, the contaminated water has been a threat to human health and ecological balance. Hence, removing these organic and inorganic effluents from the water is necessary by developing simple, sensitive and cost effective methods. Several techniques has been already implemented to remove the inorganic contaminants of water such as flocculation, bio-sorption, reverse osmosis, adsorption, solvent extraction, membrane filtration*etc.*<sup>1-6</sup>

The adsorption process is the most efficient, sensitive, simple and cost effective method to remove the heavy metal

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commercially available adsorbents were already reported in several literatures, which includes tree leaves, activated carbon, fly ash, hydroxyapatite (HAp), magnetic nanoparticles, graphene based nanocomposites, cellulose based wastes, NiC, NiO and Ni(OH)<sub>2</sub> nanorods and hydroxyapatite/magnetite.<sup>4,7-</sup> <sup>16</sup>Among these nanostructures, HAp have high specific surface area (SSA), biodegradablilty, cost effective, renewable and promising material for efficiently remove heavy metal ions from wastewater. Also, the particle geometry of HAp plays a crucial role in improving the functional properties. The HAp crystal structure includes Ca<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup> and OH<sup>-</sup> ions. The positively charged Ca<sup>2+</sup> sites are surrounded by negatively charged tetrahedral PO<sub>4</sub><sup>3-</sup> units and OH<sup>-</sup> ions occupy columns parallel to the hexagonal axis. The positively charged Ca<sup>2+</sup> ions are mainly present at a (b)-planes and negatively charged  $PO_4^{3-}$ and OH<sup>-</sup> ions are present in the *c*-planes.<sup>17</sup> These two different charges of HAp may be responsible for the adsorption of heavy metal ions from wastewater. However, these adsorbents are expensive to regenerate, difficult to dispose, recover after treatment and failed to reduce the concentration of contaminants at very low ppb levels.

ions from waste water. Hence, numerous cost effective and

Alternatively, advanced oxidation process is suitable for the oxidation of a wide range of organic compounds. Semiconducting metal oxide based heterogeneous



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photocatalysts have been proven to be of interest due to their complete elimination of organic compounds from contaminated waste water. The most intensively used photocatalysts are CeO<sub>2</sub>/Fe<sub>3</sub>O<sub>4</sub>, ZnO, WO<sub>3</sub>, SnO<sub>2</sub>-ZnO, graphene oxide/carbon nanotube, MnO<sub>2</sub>/Graphene, graphene@TiO<sub>2</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>@SnO<sub>2</sub>.<sup>18-28</sup>Among these, hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is a promising photocatalysts due to its chemically stable structure, favourable band gap (2.1-2.2 eV) to absorb photons in the UV and visible light range. However, its photodegradation is delayed due to the short lifetime of the photogenerated charge carriers (<10 ps), short hole diffusion length (2-4 nm), and poor mobility of charge carriers the production of charge carriers deep inside of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and it enhances the electron-hole pair separation causes to increase the photocatalytic efficiency.

The synthesis techniques can able to control the size and shape of the nanomaterials to decide their functional properties. Hence, sol-gel, co-precipitation, solvothermal and hydrothermal methods were explored to produce nanocomposite materials with uniform dispersibility.<sup>29-31</sup> Among these, the hydrothermal process is a well-established wet chemical approach to prepare nanocomposite materials with desired morphologies. The preparation of different morphologies of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles through simple hydrothermal technique such as flower-like microspheres, hollow spheres, cantaloupe-like superstructures, nanoflowers and dendrites were already reported.<sup>20,23,32</sup> Already the researchers reported the uniform dendritic structures of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>havebetter photocatalytic as well as superparamagnetic behavior.

In general, dendritic hematite  $(\alpha - Fe_2O_3)$  nanoparticles are very efficient to remove organic pollutants from contaminated industrial waste water due to their high surface area and catalytic property. But, it has a very low sorption capacity due to their poor electrostatic attraction. Alternatively, the nanostructured HAp mineral are effective adsorbent to remove inorganic hazardous materials from wastewater and has a minimum catalytic activity. Hence, preparing the nanocomposite of these two materials can offer the probability to improve the photocatalytic activity as well as the adsorption capacity. Based on that, we have decided to prepare the nanocomposites of HAp/a-Fe<sub>2</sub>O<sub>3</sub> to remove the organic and inorganic effluents from wastewater.

Herein, we report a facile cost effective hydrothermal process to prepare the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and it's composite with HAp. These nanocomposites were systematically studied by different analytical techniques to identify their structural, morphological and functional properties. The HAp in the nanocomposite has very good adsorption capability and the Fe<sub>2</sub>O<sub>3</sub> has feeble magnetic effect. Thereby, we explored the prepared nanocomposite as an efficient photo catalyst for degrading the organic pollutants as well as an adsorbent for removing the heavy weight metal ions from aqueous solutions. Also, its larger specific surface area helps faster degradation and adsorption of methyl violet (MV) and Pb(II) ions. The effects of adsorbate pH, contact time and initial concentrations of Pb(II) adsorption process were also investigated. The

kinetics of the process was also very well examined by fitting the experimental data with theoretical models.

#### 2. Experimental

#### 2.1 Reagents

Calcium chloride dihydrate (CaCl<sub>2</sub>.2H<sub>2</sub>O), sodium creatine phosphate dibasic tetrahydrate, potassium hexacyanoferrate (II) trihydrate (K<sub>4</sub>Fe(CN)<sub>6</sub>.3H<sub>2</sub>O) were purchased from Sigma-Aldrich and ammonium hydroxide (NH<sub>4</sub>OH), sodium hydroxide (NaOH), hydrochloric acid (HCl), 4-(2pyridy lazo)resorcinol (PAR) reagent, acetone, methyl violet and ethanol were purchased from Himedia, India. All the reagents and chemicals were used without further purification. **2.2 Synthesis of hydroxyapatite nanoparticles on dendritic**  $\alpha$ -**Fe<sub>2</sub>O<sub>3</sub>** 

A simple hydrothermal process was used for the preparation of hydroxyapatite (HAp) nanoparticles on dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. In a typical synthesis, 0.5 M of K<sub>4</sub>Fe(CN)<sub>6</sub>.3H<sub>2</sub>O was dissolved in 20 mL of deionized water with constant stirring and represented as Solution A. Further, 50 mM of CaCl<sub>2</sub>.2H<sub>2</sub>O was dissolved in 10 mL of deionized water to form Solution B and sodium creatine phosphate dibasic tetrahydrate was dissolved in 10 mL of deionized water to form Solution C. Subsequently, Solution C was added drop wise to Solution B with constant stirring at room temperature and pH was adjusted to 10.5 by adding the ammonium hydroxide (30 %) with vigorous stirring for 30 min. Further, the above translucent mixed solution was added to Solution A with constant stirring for another 30 min at room temperature. The resulting solution was transferred to a Teflonlined stainless steel autoclave and kept in an oven at 180 °C for 12 h for hydrothermal reaction and slowly cooleddown to room temperature naturally. Finally, the obtained brown colour precipitate was washed several times with double distilled water and followed by ethanol and dried at 70 °C under vacuum for 24 h before any characterization.

#### 2.3. Characterization

The powder X-ray diffraction (XRD) pattern were acquired at room temperature using an analytical X'Pert-Pro X-ray diffractometer equipped with Cu K $\alpha_1$  radiation ( $\lambda$ = 1.5406 Å) for a scanning range of 20 to 80°. The average crystallite sizes were estimated from the X-ray line broadening using the Scherrer formula. The Fourier transform infrared spectra were recorded in a Bruker Tensor 27 FTIR spectrometer. The field emission scanning electron microscopy (FESEM) images were recorded using a FEI Quanta-250 FEG coupled with EDX spectroscopy. Raman scattering was performed on a JY-1058 Raman spectrometer using a 520 nm laser source. UV-Visible spectral analysis was done by using Josco V-650 spectrophotometer. The specific surface area and pore sizes were determined by BET-N<sub>2</sub> adsorption for the nanostructures using a micro meritics ASAP 2020 surface area analyzer.

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#### 2.4 Evaluation of photocatlytic activity

The photocatlytic activities of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp on leaf-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures were estimated bv decolourizing the methyl violet (MV) dyes under ultraviolet (UV) irradiation at room temperature. In the process, 20 ppm of MV was dissolved in 100 ml of water and 10 mg of photocatalyst. Further, the prepared solution was stirred for 30 min at room temperature to achieve adsorption equilibrium and uniform dispersibility. The solution was further exposed to ultraviolet irradiation in an 18 W mercury lamp with a 365 nm cut-off filter at room temperature. Meanwhile, the suspension was magnetically stirred during an irradiation using magnetic stirrer. At periodic intervals, 3 mL of solution was withdrawn and magnetically separated to remove the photocatalyst nanoparticles. The remaining dye concentration in the supernatant solution was analysed by measuring the absorption intensity of MV by UV-visible absorption spectroscopy at a wavelength of 530 nm.

#### 2.5 Sorption Studies

The Pb(II) adsorption process was executed for the pure  $\alpha$ - $Fe_2O_3$  and HAp on dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> adsorbents to determine the optimum adsorption conditions. A typical batch mode adsorption experiments were carried out with HAp/a-Fe<sub>2</sub>O<sub>3</sub> nano adsorbent at room temperature. The effect of pH on the adsorption capacity  $(Q_0)$  was investigated in the range from 2 to 10 by using Pb(II) solution prepared from the standard 1000 mg/L stock solution to the preferred concentrations of 20, 40 and 60 mg/L through sequential dilution. The pH was adjusted by using sodium hydroxide (NaOH) or hydrochloric acid (HCl) solutions. The resultant mixture solutions were transferred to 50 mL standard measuring flask and stirred on a thermostatic mechanical shaker operating at a constant speed of 300 rpm. Finally, the sample was withdrawn from the shaker at predetermined time intervals and the supernatant was collected by applying an external magnetic field. The resultant clear solution was used to estimate the lead absorption by using spectrophotometric analysis. The supernatant solution of 50 mL was taken in a test tube and added 10 mL of ammoniaammonium chloride buffer solution (16.9 g of NH<sub>4</sub>Cl + 123 ml of liquor ammonia mixed with 250 mL of H<sub>2</sub>O) and followed by the addition of 1 mL of 0.01 % solution of 4-(2- pyridy1azo) resorcinol (PAR) reagent for the analysis. This was further incubated at 35 °C for colour development and finally the absorbance of the samples was measured in a UV-visible spectrophotometer in the wavelength of 520 nm.

#### 3. Results and discussion

#### 3.1 Structural and morphological analyses

The dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp nanoparticles dispersed on dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hierarchical architectures were prepared by a hydrothermal process. K<sub>3</sub>[Fe(CN)<sub>6</sub>] as a single complex precursor and it plays a vital role in the formation of dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.



Fig.1 Schematic illustration for the formation mechanism of HAp dispersed on dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hierarchical architecture by controlled growth along six crystallographically equivalent directions  $\langle 10\overline{10} \rangle$  and Pb (II) adsorption and MV photo degradation

The following three steps during the hydrothermal process direct the formation of dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Initially, the [Fe (CN)<sub>6</sub>]<sup>3-</sup> ions resolve slowly to Fe<sup>3+</sup> ions and thereafter these ions are successively hydrolyzed to form FeOOH or Fe(OH)<sub>3</sub>. Finally, the resulting FeOOH or Fe(OH)<sub>3</sub> are decomposed to form a dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

$$[Fe(CN)_6]^{3-} \rightarrow Fe^{3-} \rightarrow FeOOH / Fe(OH)_3 \rightarrow \alpha - Fe_2O_3$$
 (1)

Fig.1 shows the proposed formation mechanism for HAp nanoparticles dispersed on the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hierarchical architecture by controlled growth along the six crystallographically equivalent directions  $(10\overline{1}0)$  and for the wastewater treatment (Pb (II) adsorption and MV photodegradation). The formation of dendritic architecture starts from  $(10\overline{1}0)$  six crystallographic directions of the seed crystal at a growth rate much faster than the other six crystallographic directions. Dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> consists of long central trunk along the <1010>crystallographic direction and sub-branches formed along the <0110>and <1010>crystallographic directions, causes the complete formation of a hierarchical and symmetric dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> structure.

In contrast, the HAp nanoparticles were grown on the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> by a hydrothermal process at 180 °C for 12 h. In this process, creatine phosphate (CP) as an organic phosphate (PO43-) source for the preparation of HAp nanoparticles on dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The hydrothermal temperature plays an important role in releasing the phosphate  $(PO_4^{3-})$  ions from CP molecule and improves the crystallinity and nucleation growth of HAp on dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> structure. During the hydrothermal process, the CP molecules hydrolyze to release phosphate  $(PO_4^{3-})$  ions as well as creatine molecules. The  $(PO_4^{3-})$  ions further react with  $Ca^{2+}$  ions via electrovalent bonds and pH was adjusted. Finally, the HAp nuclei were formed on the surfaces of dendritic a-Fe<sub>2</sub>O<sub>3</sub> hierarchical architecture. The obtained products were applied as a photocatalyst for the degradation of MV dye as well as adsorbent for Pb(II) ions from aqueous solutions.



Fig.2 X-ray diffraction pattern for (a)  $\alpha\text{-}Fe_2O_3$  and (b) HAp/ $\alpha\text{-}Fe_2O_3$  nanocomposite

The phase analysis and crystallinity of the as-prepared samples were identified by using X-ray diffraction (XRD) pattern. Figure 2 shows the powder X-ray diffraction pattern for the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp on dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The diffraction peaks in Fig. 2(a) for the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>were very well matches with a pure rhombohedral crystal structure [JCPDS # 89-8104]. The maximum intensity peak at 35.45° corresponds to (110) plane of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can be used to estimate the average crystallite size using Scherrer formula and the estimated size is 30 nm.Figure 2(b) shows the XRD pattern for HAp nanoparticles on  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. It shows the dual phases of pure HAp (JCPDS # 09-0432) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (JCPDS #89-8104). The XRD pattern confirms the formation of well crystallized hexagonal HAp and rhombohedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> without any impurity phase.



Fig.3 FTIR spectra for dendritica-Fe\_2O\_3 and HAp/a-Fe\_2O\_3 nanocomposite

The formation and identification of functional group present in the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite are further supported by the FTIR analysis. FTIR spectra in Fig.3 shows the sharp intense peaks at 466 and 572 cm<sup>-1</sup>corresponds to the stretching vibration of Fe<sup>3+</sup>-O<sup>2-</sup> bond in the FeO<sub>4</sub> tetrahedron and FeO<sub>6</sub> octahedron respectively. Three intense peaks observed at 3445, 2923 and 1634 cm<sup>-1</sup> are corresponds to the asymmetrical stretching vibration and deformation vibration of physically adsorbed water molecule on the as-prepared samples respectively.The characteristic absorption band of OH<sup>-</sup> stretching mode occurs at 3574 and 632 cm<sup>-1</sup>. The intense peak at 568 and 602 cm<sup>-1</sup> are due to the bending vibrations of the O-P-O in the PO<sub>4</sub><sup>3-</sup> groups. The asymmetric stretching vibrations of the P-O in the PO<sub>4</sub><sup>3-</sup> groups are at 1099 and 1037 cm<sup>-1.31-33</sup>

The Raman spectroscopy has been adopted to complete the structural analysis of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite. The Raman spectra in Fig. 4 shows the sharp characteristic peak at 947 cm<sup>-1</sup> corresponds to the symmetric stretching  $V_1$  (PO<sub>4</sub><sup>3-</sup>) corresponds to free tetrahedral phosphate ions. The peaks at 416, 574 and 1048 cm<sup>-1</sup> are attributed to  $V_2$ symmetrical bending vibration of  $PO_4^{3-}$ ,  $V_3$  asymmetrical stretching mode of  $PO_4^{3-}$  and  $\mathcal{V}_4$  anti-symmetric bending of  $PO_4^{3-}$  modes. Raman spectra of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> can exhibit five characteristic peaks at 225, 290, 403, 607 and 1035 cm<sup>-1</sup>. The peak at 225 cm<sup>-1</sup> corresponds to A<sub>1g</sub> mode, which involves movements of iron cations along the crystallographic c-axis. The other peaks observed at 290, 403 and 607 cm<sup>-1</sup>are associated with Eg mode, which can be observed as a symmetric breathing mode of the O atoms correlated each iron cations in the plane perpendicular to the *c*-axis.<sup>34</sup>



Fig. 4 Raman spectra for pure HAp,  $\alpha\text{-}Fe_2O_3$  and HAp/ $\alpha\text{-}Fe_2O_3$  nanocomposite



Fig. 5FESEM images of (a-c)  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (d-f) HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite with different magnifications and (g-j) FESEM elemental mapping and (k and l) EDAX micrographs of HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite

Morphology of the hydrothermally synthesized a-Fe<sub>2</sub>O<sub>3</sub> and HAp/a-Fe<sub>2</sub>O<sub>3</sub> nanocomposite were examined by using field emission scanning electron microscopy (FESEM). Figure 5(a-c) shows the low and high magnification images of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures. It shows the dendrite-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures having an average trunk length of 1 µm long central trunk with the secondary branches of 80 nm. The higher magnification image in Fig.5(c) shows the clear and well defined dendritic structure. Fig.5(d-f) shows the low and high magnification images of  $HAp/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite. The distribution of IIAp nanoparticles on the dendritic a-Fe<sub>2</sub>O<sub>3</sub> nanostructures can clearly visible in Fig. 5(e) and (f). The HAp particles are very well distributed on the long central trunk as well as the sub-branches of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The EDAX mapping in Fig. 5(g-j) collected in Ca, P, Fe, O edges confirms the uniform and well distribution of the elements. The EDX spectrum of dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite is shown in Fig. 5 (k and l) reveals the presence of Fe, O, Ca, and P in the sample and no other impurities were detected.

Iron oxides are well-known magnetic materials and α-Fe<sub>2</sub>O<sub>3</sub> is not an exception. Bulk a-Fe<sub>2</sub>O<sub>3</sub> is reported to have canted anti-ferromagnetic order. a-Fe2O3 nanoparticles are reported to be weakly ferromagnetic at temperatures down to 5 K.It has been realized that the magnetic properties of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructure is highly dependent on the morphology and size. Magnetic hysteresis loop for the as-prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures and the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/HAp nanocomposite are recorded in a vibrating sample magnetometer (VSM) at room temperature. Fig.S1 shows the magnetic hysteresis loop for the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite measured at room temperature. The saturation magnetization  $(M_s)$ , coercivity  $(H_c)$  and remanent magnetization  $(M_r)$  estimated from the *M*-*H* curves of both samples are listed in Table S1. The values confirm the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> shows weak ferromagnetism at room temperature. Fig. S1(b) shows the M-H

curve for  $HAp/\alpha$ - $Fe_2O_3$  nanocomposite. There is a small change in the magnetic properties were observed compared to the dendritic  $\alpha$ - $Fe_2O_3$ . The increase in the coercivity is due to the influence of OH and water molecules on the surface of the  $HAp/\alpha$ - $Fe_2O_3$  samples.

The specific surface area, pore volume and pore size distribution of the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/a-Fe<sub>2</sub>O<sub>3</sub>nanocomposite were further estimated from the nitrogen physisorption (adsorption-desorption) isotherms. Fig.6 shows the BET surface area and corresponding BJH pore size distribution plots. The adsorption-desorption isotherms confirm the type IV isotherm loop at a relative pressure between 0 to1. Both the samples display mesoporeswith the pore size distributions in the range of 5 -20 and 4 nm for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/a-Fe2O3nanocomposite using Barrett-Joyner-Halenda (BJH) calculations. The specific surface area (SSA) calculated by BET theory are 40.5 and 80.7  $m^2g^{-1}$  for the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $HAp/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> respectively. The observed high specific surface area of the HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite might be due to the presence of smaller grain size of the HAp nanoparticles.



Fig. 6Nitrogen adsorption/desorption isotherms and pore-size distribution (inset) for (a) dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (b) HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite.



Fig. 7 High resolution XPS spectra for  $HAp/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite (a) Fe 2P, (b) O1s, (c) Ca2p and (d) P2p

The high resolution XPS was performed to analyze the chemical structure and states of Fe, O, P and Ca in the HAp/a-Fe<sub>2</sub>O<sub>3</sub> nanocomposite and the corresponding spectra are shown in Fig.7. The XPS spectrum of Fe 2P exhibits three dominant peaks at 710.08, 719.1 and 724.6 eV corresponds to Fe 2P<sub>3/2</sub>, satellite and Fe  $2P_{1/2}$  respectively, which confirms the presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as shown in Fig.7(a). The spectrum for O1s in Fig.7(b) shows two intense peaks at 529.84 and 531.84 eV, associated with anionic oxygen in hematite phase. Fig.8(c) shows the peak at 133 eV for the presence of phosphate group (P2p) in the HAp. Fig.8(d) shows the high resolution XPS spectrum of Ca2p demonstrate two prominent peaks at 347.5 and 350.4 eV corresponding to the  $Ca2p_{3/2}$  and  $Ca2p_{1/2}$ , respectively. Therefore, the high resolution XPS spectrum proves that the HAp nanoparticles formed on surfaces of a-Fe<sub>2</sub>O<sub>3</sub>.<sup>30&31</sup>

The optical property of the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposites are most important for the evaluation of their photocatalytic activity. The optical property of the HAp, dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite were investigated at room temperature with UV-visible spectrophotometer. Fig.S2 (a&b) shows the UV-Visible spectra for the HAp, dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite. It exhibits an intense peak at 307 nm and a broad hump-like shoulder in the wavelength region of 250-400 nm. These absorption peaks are mainly observed in the ultraviolet region with peaks at 295 and 307 nm for dendritic a- $Fe_2O_3$  and  $HAp/\alpha$ - $Fe_2O_3$  nanocomposite respectively. Generally, the adsorption bands in the ultraviolet region from 250 to 400 nm are associated to the ligand-to-metal charge transfer (direct transitions) and partlyfrom the contributions of the Fe<sup>3+</sup> ligand field transition<sup>6</sup>A<sub>1</sub> $\rightarrow$ <sup>4</sup>T<sub>1</sub> (<sup>4</sup>P) at 290-310 nm,  ${}^{6}A_{1} \rightarrow {}^{4}E$  (<sup>4</sup>D) and  ${}^{6}A_{1} \rightarrow {}^{4}T_{2}$  (<sup>4</sup>D) at 360-380 nm and  ${}^{6}A_{1} \rightarrow {}^{4}E$ (<sup>4</sup>G) at 390 nm. In a visible region (400-600), the absorption bands near 430 nm are corresponding to  ${}^{6}A_{1} \rightarrow {}^{4}E, {}^{4}A_{1}$  ( ${}^{4}G$ )

ligand field transitions of Fe<sup>3+</sup>.Furthermore, the regions from 600 to 750 nm correspond to  ${}^{6}A_{1} \rightarrow {}^{4}T_{2}$  (<sup>4</sup>G) ligand field transitions of Fe<sup>3+</sup>. As demonstrated in Fig.S2 (a&b), the electronic transition for the charge transfer in the wavelength region 250-400 nm dominates the optical absorption features of the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposites. Therefore, dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanomaterials have been used widely as ultraviolet ray absorbents for their broad adsorption in ultraviolet region from the electron transmission of Fe-O.<sup>35,36</sup>

#### 3.2. Photocatalytic properties

The photocatalytic performances of the materials strongly depend on their size, shape, crystallanity and chemical composition. The photocatalytic performance of the dendritic  $\alpha$ - $Fe_2O_3$  and  $HAp/\alpha$ - $Fe_2O_3$  nanocomposite were evaluated using methyl violet (MV) dye under UV light irradiation ( $\lambda$ =365 nm) with various time intervals by measuring the absorbance spectra using UV-Visible spectrophotometer. The absorption spectra in Fig.8(a,b) shows the degradation of methyl violet was very stable in the absence of photocatalyst under UV light irradiation. Meanwhile, no obvious degradation was obtained in the dark, even in the presence of photocatalyst. The absorption of methyl violet was used to occur at 575 nm for the degradation process. Fig.8(a) shows the photocatalytic performance of the dendritic a-Fe<sub>2</sub>O<sub>3</sub> nanostructure for the degradation of methyl violet with UV light irradiation for various time durations. The intensity of the absorbance peaks was gradually decreases as the exposure time increases and completely disappears after 125 minutes. The absorption spectra in Fig.8(b) show the photocatalytic performance of the HAp/a-Fe<sub>2</sub>O<sub>3</sub> nanocomposite. It exhibits the rapid degradation and thereby the intensity of the absorbance peak was decreases rapidly and completely disappears within 75 minutes.

Therefore, the photodegradation rates of the HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite are much superior to the dendritic $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The degradation rate (C/C<sub>o</sub>) for the blank, dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite for a period of time is shown in Fig. 8(c). It shows the significant increase in the rate of degradation for the HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite for the methyl violet under UV irradiation. The observed increase in the photocatalytic activity of the HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> might be due to their enhanced surface area, pore size, band gap and UV light adsorption behaviour. The photodegradation mechanism explained based on the literatures and the principles of oxidative decomposition is shown in Fig. 8(d).<sup>24,25&26</sup>

In general, methyl violet dye degradation mechanism could be explained by the electron-hole (e<sup>-</sup>-h<sup>+</sup>) separation between conduction and the valance band and high specific surface area of dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. During the UV irradiation, the valance band electrons are excited to conduction band resulting electron-hole pairs are generated on the surface of the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. It may be simply trapped by the H<sub>2</sub>Oto form active hydroxyl radicals (OH) and superoxide (O<sub>2</sub><sup>-</sup>, HO<sub>2</sub><sup>-</sup>). These OH and superoxide (O<sub>2</sub><sup>-</sup>, HO<sub>2</sub><sup>-</sup>) have been considered as oxidative species and are usually determine the degradation of various organic dyes under UV light irradiation.



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**Fig. 8** UV-visible absorbance spectra forphotodegradation of MV in the presence of different catalyst, (a) pure dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, (b) HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite, (c) photocatalysis degradation rates of MV and (d) schematic illustration for the principle of oxidative decomposition of MV

The following steps are involved for the generation of hydroxyl radicals (OH) and superoxide  $(O_2^{-}, HO_2^{-})$  during the photodegradation of methyl violet.

$$\alpha - \operatorname{Fe}_2 \operatorname{O}_3 + h \upsilon \to \alpha - Fe_2 \operatorname{O}_3(e^- - h^+)$$
(2)

$$h^{+} + H_{2}O \rightarrow {}^{\bullet}OH + H^{+}$$
(3)

$$e - O_2 \rightarrow O_2^-$$
 (4)

$$O_2^- + MV \to MV^{+\bullet} - O_2 \tag{5}$$

$$^{\bullet} OH + M V^{+ \bullet} \rightarrow CO_{2} + H_{2}O$$
(6)

Based on the above degradation mechanism, the high surface area of dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sufficiently produces active oxygen radicals which are basically responsible for the degradation of methyl violet. Meanwhile, the hydroxyapatite supported dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalyst exhibits higher degradation efficiency than the dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. This may be due to HAp in the composite produces sufficient amount of O<sub>2</sub><sup>---</sup> species under UV radiation. It is already reported that the oxygen radicals were produced when the HAp placed on the UV light irradiation and sufficient amount of O<sub>2</sub><sup>---</sup> species cause to degrade methylene violet.<sup>35-38</sup>Therefore, the heterogeneous catalyst HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite with high surface area exhibits high degradation of methyl violet under UV-light irradiation due to the generation of oxy-radicals (O<sub>2</sub><sup>---</sup>, HO<sub>2</sub><sup>--</sup> and OH) on the surface.

#### 3.3Pb(II) Adsorption

The dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite are well known and an effective adsorbent to remove heavy metals and hazardous materials from wastewater. The present study is to explore the lead (II) (Pb(II)) adsorption ability of those materials from aqueous solution. The removal efficiency of the dendritic a-Fe<sub>2</sub>O<sub>3</sub> and HAp/a-Fe<sub>2</sub>O<sub>3</sub> nanocomposite were studied by varying the pH, initial concentration of the metal ions and contact time. All these parameters were optimized to find out the removal efficiency of Pb(II) ions from aqueous solution with assisted kinetics and adsorption isotherms. Fig.9(a)shows the effect of pH on the adsorption of Pb(II) ions from aqueous solution. The pH is a significant parameter for heavy metal adsorption due to its impact on the solution chemistry of the metal ions and surface charge of adsorbents. The Pb(II) adsorption behaviour of dendritic a-Fe<sub>2</sub>O<sub>3</sub> and HAp/a-Fe<sub>2</sub>O<sub>3</sub> nanocomposite were investigated by varying the range of pH from 2 to 10 in the adsorbent concentration of 10 mg/g with initial concentration of adsorbate 20 mg/L and the contact time 120 min. The results show the adsorption capacity of Pb(II) is 10 and 50 % for dendritic  $\alpha$ - $Fe_2O_3$  and  $HAp/\alpha$ - $Fe_2O_3$ , respectively at pH 2. The increase in the pH to 4 correspondingly increases the adsorption capacity to 24 and 97.5 % for dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.



Fig. 9 Adsorption effect of pH and contact time for the Pb(II) with the initial concentration of 20 mg/L. Dosage of adsorbent is 10 mg/g, (a) effect of pH and (b) effect of contact time of the  $HAp/\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

 Table 1. Summary of the Maximum Pb(II) removal capacities of different adsorbents

S.No	Adsorbent	Adsorption	Reference
		Capacity	
		(mg/g)	
1	HAp/a-Fe <sub>2</sub> O <sub>3</sub>	754.14	Present
			Study
2	Tree leaves	58.81	4
3	Hydroxyapatite from egg	500	9
	shell		
4	Hydroxyapatite	357.14	10
5	Graphene nanosheets	35.46	12
6	NiC composite	21.4	14
	nanostructures		
7	Nanorods NiO and	32 and 28	15
	Ni(OH) <sub>2</sub>	26 and 33	
	Dandelion-like NiO and		
	Ni(OH) <sub>2</sub>		
8	Hydroxyapatite/magnetite	598.8	16

The experimental data were fitted using the Lagergren's first order rate equation and pseudo second order kinetic model to determine the adsorption rates of Pb(II) ions on HAp/a-Fe<sub>2</sub>O<sub>3</sub>nanocomposite. The detailed description of Lagergren's first order and pseudo second order kinetic model were presented in supporting information. The values of  $q_e$  and  $K_l$ , were calculated from the slope and intercept of the plots of  $log(q_{e}, q_{t})$  versus time (t) in the Lagergren's first order rate equation and the correlation coefficient of 0.9676, 0.9694 and 0.9665 were obtained for 20, 40 and 60 mg/L, respectively as shown in Fig. S3(a). In the pseudo second order kinetic model, the values of  $K_2$  and  $q_e$  were calculated from the plots of t/qversus t as shown in Fig. S3(b). The  $q_{e,cal}$  and  $q_{e,exp}$  values are very close to each other and the correlation coefficient of 0.9997, 0.9985 and 0.9986 are corresponds to 20, 40 and 60 mg/L. The pseudo-first order kinetics, the experimental data significantly deviates from linear fit and this was evident by the low correlation values. On the basis of the above results indicates the adsorption follows the pseudo-second order kinetic model.

The adsorption isotherms were mathematical analysis which used to designate the diffusion of the adsorbate species between solid and liquid phases. The adsorption capacity  $(Q_o)$  of Pb(II) on the HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was used to determine the characteristic adsorption constants by using Langmuir and Freundlich models. The observed experimental data were fitted with these models to describe the adsorption performances of heavy weight metal ions on the adsorbents. The Langmuir and Freundlich isotherms constants and correlation coefficients were determined using the linear method which consists of plotting  $C_e/q_e$  versus  $C_e$  and  $\log q_e$  versus  $\log C_e$  respectively. All the resulting parameters are presented in the Table S2. The maximum adsorption efficiency  $(Q_o)$  observed based on Langmuir model was 754 mg/g for the HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite with the correlation coefficient (R<sup>2</sup>) of 0.8316

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as shown in Fig. S3(c).Fig. S3(d) shows the data fitted with Freundlich isotherm and the value of adsorption isotherm constants 1/n and R<sup>2</sup> are 0.5737 and 0.9841 respectively and the empirical parameter 1/n value is in the range 0.1 < 1/n < 1 confirms the adsorption process is favorable. The Freundlich isotherm is favorable for adosrption of Pb(II) ions from aqueous solution by HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite confirm their good heterogeneous adsorption capacity. The Pb(II) removal capacity of the HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite was higher than that of the reported values as presented in Table 1. <sup>9,10,12-16&39-41</sup>

The HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite provides large adsorption sites due to their high specific surface area and higher pore size distributions. Therefore, the adsorption capacities were relatively more and Pb(II) ions were easily adsorbed on the surface as well as pores of the adsorbent. Another important advantage of the present adsorbent is their easy desorption due to the magnetic effect and thereby and it can be easily recycled without any membranes with high recovery ratio.

#### - 4. Conclusion

In summary, the nanoparticles of HAp on dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with highly mesoporous structure have been successfully prepared by simple hydrothermal process. The prepared dendrites have 1 µm length with the secondary branches of 80 nm. The nanocomposite had a high specific surface area of 80.7 m<sup>2</sup>g<sup>-1</sup> with weekly ferromagnetic at room temperature. It also had an extremely fast degradation of methyl violet and higher adsorption capacity for Pb(II) ions from aqueous solutions. The adsorption kinetics follows pseudo-second-order model and well defined by Freundlich isotherms. The maximum adsorptions capacity of 754.14 mg/g was observed at lower pH value of 4. In future, these novel HAp/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposites have been used as very good photocatalyst as well as adsorbent for environmental remediation and simultaneously remove organic and inorganic pollutants from waste water.

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